

CHAPTER V
GROWTH OF SINGLE-WALLED CARBON NANOTUBES BY
DISPROPORTIONATION OF CO OVER Co-Re/SiO₂ CATALYSTS*

5.1 Abstract

A series of silica supported Co-Re catalysts was prepared for the synthesis of single-walled carbon nanotubes (SWNTs) using carbon monoxide disproportionation at 750-950°C. The carbon products were characterized by Raman spectroscopy, temperature programmed oxidation (TPO) and transmission electron microscope (TEM). The effects of the molar ratio of Co to Re, reduction temperature, and reaction temperature were investigated. The characterization results of Co-Re catalysts suggest that good quality of SWNTs can be obtained by using partially reduced and completely reduced cobalt-rhenium oxide. It was found that the synergism of Co and Re in the catalytic production of SWNTs leads to high selectivity of SWNTs.

5.2 Introduction

In the production of single-walled carbon nanotubes (SWNTs) by the disproportionation of carbon monoxide, it has been found that Co is an active catalyst but the Co alone as a catalyst on silica support is not highly selective towards SWNTs [1]. When Co and Mo are simultaneously present, particularly when the Mo content is in excess, the selectivity towards SWNTs is significantly enhanced. In addition, it has been found that the interaction between Co and Mo is critical for providing good catalytic performance, because the role of Mo is to stabilize the Co⁺² ions in the form of a superficial Co molybdate-like structure. Therefore, the well-dispersed Co⁺² species is not reduced to form larger metallic Co clusters during the reduction treatment of the catalyst [2]. Recently, the stabilization of Co⁺² ions in a Co tungstate-like phase has been observed on the silica-supported Co-W catalyst for the SWNTs synthesis [3]. From the successful combination of Co-Mo and Co-W

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systems, it has been proposed that the SWNTs selectivity strongly depends on the stabilization of Co species in a non-metallic state before exposed to CO. In other applications, the Co-based catalysts are commonly employed in the Fisher-Tropsch synthesis for the conversion of CO and H₂ into hydrocarbons and water. However, the addition of Re as a promoter to the Fisher-Tropsch catalyst exhibits the improvement on the formation of long-chain *n*-paraffins, but the synergism between Co and Re is still unclear [4, 5].

In this study, the use of silica-supported Co-Re catalytic system for the production of SWNTs by disproportionation of CO was investigated. The catalysts were characterized by temperature-programmed reduction (TPR). The effects of pretreatment, reaction temperature, and catalyst formulation on the yield and selectivity towards SWNTs were observed by using Raman spectroscopy, temperature programmed oxidation (TPO), and transmission electron microscope (TEM).

5.3 Experimental Section

5.3.1 Materials

5.3.1.1 Metal Precursors and Catalyst Support

There are 2 metal precursors used in this study, Co precursor in the form of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) with 98% purity and Re precursor in the form of ammonium perrhenate (NH₄ReO₄) with 99% purity. Silica gel (SiO₂) was used as a catalyst support and it has particle sizes in the range of 70-230 mesh (62 – 210 μm), average pore diameter of 6 nm, a BET surface area of 480 m²/g, and a pore volume of 0.75 cm³/g. All the metal precursors and catalyst support were supplied by Sigma-Aldrich Co. Ltd. All chemicals were used as received without any purification.

5.3.1.2 Gases

Air zero with a purity of 99.99% was used in the calcination of the catalyst. 2% of oxygen in helium gas was used as an oxidizing agent in temperature-programmed oxidation (TPO). 5% of hydrogen in nitrogen gas was used as a reducing agent in the temperature-programmed reduction (TPR). Helium was used as a purge gas in the TPO and in the heating step of the reaction experiments. Nitrogen with a purity of 99.99 % was used as purge gas in the TPR experiment. Hydrogen with a purity of 99.99 % was used in the pre-reduction step of the SWNTs synthesis. All of the above gases were supplied by Thai Industrial Gas Co. Ltd. Carbon monoxide gas with a purity of 95% was obtained from Airgas Inc. It was used as carbon source for the SWNTs synthesis.

5.3.2 Methodology

5.3.2.1 Catalyst Synthesis Procedure

Co, Re, and Co-Re catalysts supported on silica gel were prepared by the impregnation of aqueous cobalt nitrate and ammonium perrhenate solutions to obtain bi- or monometallic catalysts. In the series of bimetallic catalysts, the amount of Co was kept constant at 1 wt %, while the amount of Re was varied to obtain the Co:Re ratios of 2:1, 1:1, and 1:4. Two monometallic catalysts were prepared at the metal loadings of 1 wt % Co and 3.2 wt % Re. The SiO₂ support was impregnated using a liquid/solid ratio of 0.6 cm³/g. After the impregnation step, the samples were first dried in air at room temperature for 2 h, then dried overnight in oven at 120°C, and finally calcined in the flow of dry-air at 500°C for 3 h.

5.3.2.2 Catalyst Characterization

The temperature-programmed reduction (TPR) experiments on the calcined catalysts were conducted in a Thermo Finnigan TPDRO 1100 equipped with a thermal conductivity detector. The system was operated by passing a continuous flow of 2% H₂ in N₂ over approximately 50 mg of the calcined catalysts, while the temperature was linearly increased at a rate of 10°C/min. The intensities of

thermal conductivity which corresponds to the amount of hydrogen consumption by the samples were plotted with the temperature.

The Raman spectra of nanotubes were recorded using a Jobin Yvon Horiba LabRam 800 equipped with a CCD detector and with the laser excitation source having a wavelength of 632 nm. The Raman spectra were obtained by using 3.0-5.0 mW laser power; 15 s integration time for each spectrum; and ten Raman spectra were averaged for each sample.

5.3.2.3 Reaction Experiments

The catalytic reaction system for synthesizing SWNTs consists of a pre-heater, a heater, a horizontal quartz tubular reactor, two pressure gauges, a temperature controller, a thermo couple, and four mass flow controllers. The experimental set-up for this system is shown in Figure 5.1 and the photo of the studied reactor system is shown in Figure 5.2.

For the production of nanotubes, 0.5 g of a calcined catalyst sample was placed in the reactor, heated in 50 cm³/min H₂ at different temperatures in the range of 500-900°C for 30 min, and then in 50 cm³/min He up to a specific reaction temperature which ranged from 750 to 950°C. Subsequently, 99.5% purity CO was introduced at a flow rate of 850 cm³/min at 5 atm for 1 h. At the end of each run, the system was cooled under the flow of He. The deposited carbon on the catalyst was characterized by the temperature-programmed oxidation (TPO) using the method described elsewhere [1], Raman spectroscopy, and transmission electron microscopy (TEM). The TEM images were obtained using a TEM (JEOL, JEM-2000FX) at 200 kV.

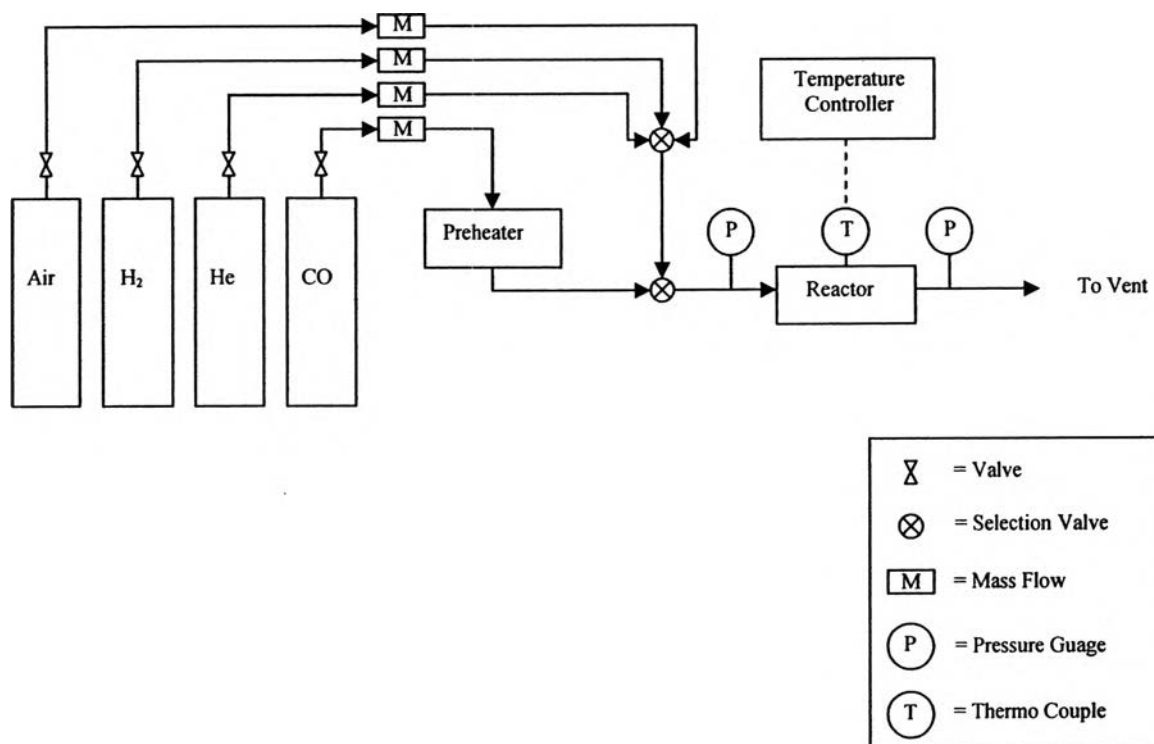


Figure 5.1 Experimental set-up of the catalytic reactor system for synthesizing single-walled carbon nanotubes (SWNTs).

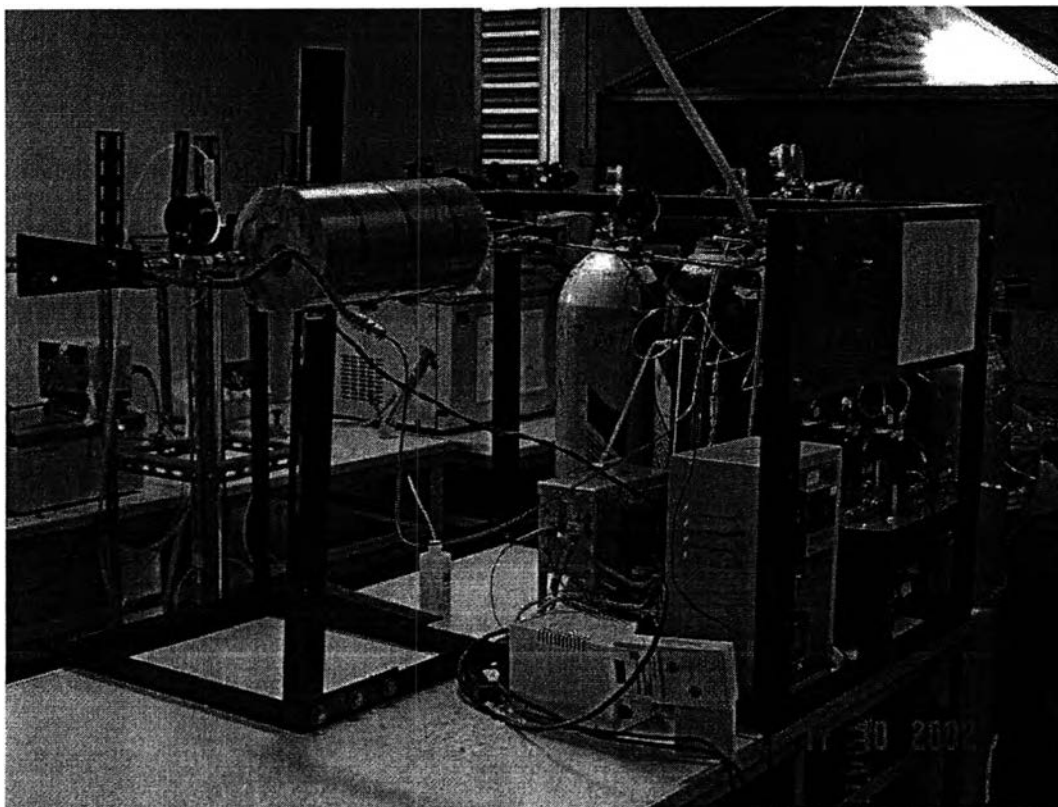


Figure 5.2 Photo of the reactor system for synthesizing single-walled carbon nanotubes (SWNTs).

5.4 Results and Discussion

5.4.1 Effect of Reduction Temperature

To investigate the effect of the reduction temperature on the yield and selectivity of SWNTs, the experiments were conducted by the pretreatment with H_2 at 500, 600, 700, 800, and 900°C over Co-Re(1:4)/SiO₂ catalyst. For the reaction step, Co was fed into the reactor at 850°C for 1 h. The normalized TPO profiles of the nanotubes samples obtained from different reduction temperatures are illustrated in Figure 5.3. For each reduction temperature, the total area under the normalized TPO profile is used to calculate the yield value of carbon product, which is defined as a weight percentage of carbon deposited per total catalyst weight.

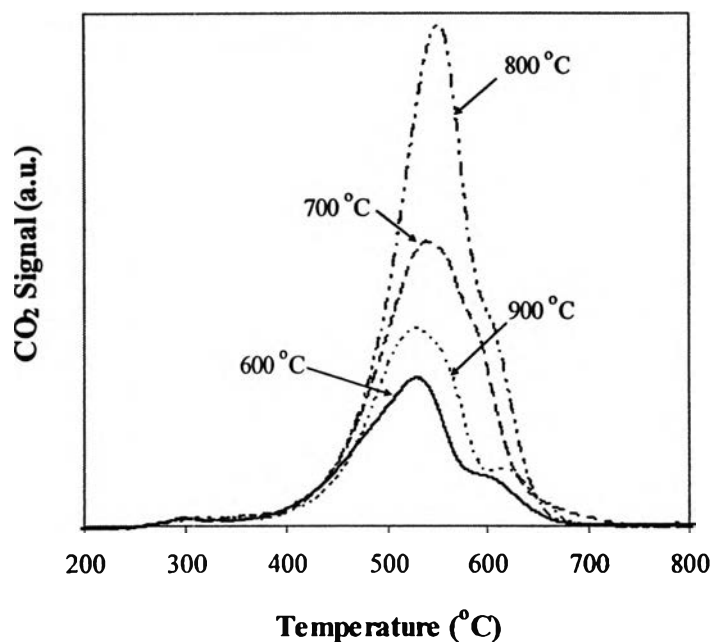


Figure 5.3 Temperature-programmed oxidation (TPO) of the carbon deposit obtained from by CO disproportionation at 850°C over Co-Re(1:4)/SiO₂ catalyst with pre-reduction at different temperatures.

As shown in Figure 5.3, the amount of carbon deposited on the Co-Re(1:4) catalyst increases with increasing reduction temperature from 600°C to 800°C. The maximum carbon yield of 5.8 wt % was obtained at 800°C. However, at a reduction temperature of 900°C, the carbon yield dramatically dropped to 2.8 wt % which may be due to the agglomeration of Co particles to form larger metallic Co particles. In addition to the TPO results, the Raman spectroscopy provides useful information about the structure of carbon nanotubes. The information about the tube diameter of SWNTs can be directly obtained from the analysis of radial A_{1g} breathing mode which occurs below 300 cm⁻¹ [6]. The information about the electronic properties of the nanotubes can be obtained from the investigation of the graphite-like tangential mode (G band), ranging from 1,400 to 1,700 cm⁻¹. Moreover, the indication on the level of disordered carbon can be obtained from the analysis of the D band at around 1,350 cm⁻¹. From the Raman spectra, qualitative measurement on the formation of undesirable forms of carbon can be estimated by comparing the

size of the D band to the G band at around $1,590\text{ cm}^{-1}$ [7]. In this work, a quality parameter has been defined and used as an indicator for the quality of carbon products.

$$\text{Quality Parameter} = \frac{G}{D+G} \times 100$$

where D and G are integrated areas of the D and G bands, respectively. A quality parameter approaching 100 represents a high-quality product. Figure 5.4 shows the Raman spectra of the carbon deposited on the spent Co-Re(1:4)/SiO₂ catalysts under different reduction temperatures. Regarding to both Raman and TPO results, the optimum reduction temperature seems to be around 800°C where the quality parameter was maximum about 85. As the reduction temperature increased up to 900°C, the quality parameter drastically dropped to 53.

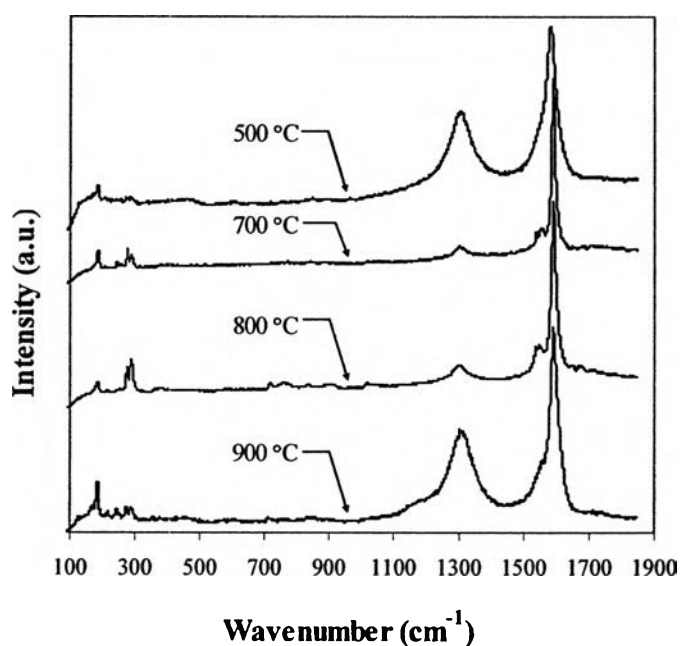


Figure 5.4 Raman spectra of the carbon deposits obtained from the CO disproportionation at 850°C over the Co-Re(1:4)/SiO₂ catalyst with different pre-reduction temperatures.

However, the TPR results of both mono- and bimetallic catalysts, Figure 5.5, demonstrated that complete reduction of metal oxides in all bimetallic

Co-Re catalysts occurred below 600°C. As a result, the optimum prereduction temperature at 800°C may lead to the conversion of Co-Re oxides into Co-Re alloy with an appropriate interaction that is necessary for the growth of nanotubes. From this observation, the stabilization of Co species occurred in the Co-Re alloy phase, which is different from what was observed on the Co-Mo/SiO₂ catalysts as previously described.

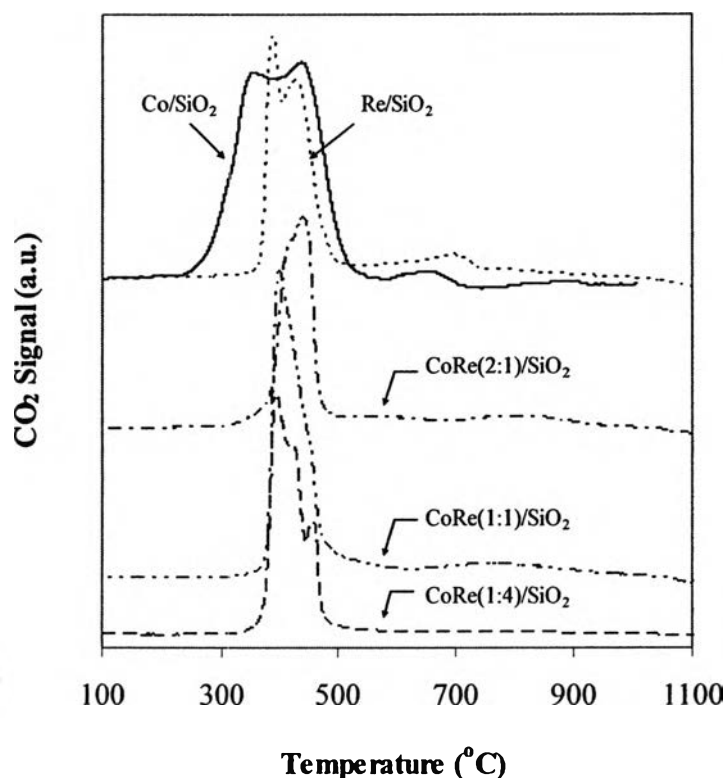


Figure 5.5 Temperature-programmed reduction (TPR) of the monometallic and bimetallic cobalt/rhenium catalysts having different molar ratio of Co to Re.

5.4.2 Effect of Reaction Temperature

Co-Re(1:4)/SiO₂ catalyst was selected to study the effect of reaction temperature on the carbon yield. In this study, the catalyst was pretreated in H₂ at 800°C and the reaction experiments were conducted at three different reaction temperatures: 750, 850, and 950°C. The normalized TPO profiles obtained from the spent catalyst samples at different reaction temperatures are illustrated in Figure 5.6.

Interestingly, as the reaction temperature varied from 750°C to 950°C, the maximum carbon yield (5.6 wt %) was observed at a reaction temperature of 850°C. At a higher or lower than the optimum reaction temperature of 850 °C, a larger amount of either disordered carbon (oxidation peak < 400°C) or graphitic carbon such as multi-walled carbon nanotubes (oxidation peak > 600°C) were formed. However, in the case of 950°C reaction temperature, the fraction of MWNTs increased due to the rapid agglomeration of Co metallic particles to larger clusters, known as the sintering effect.

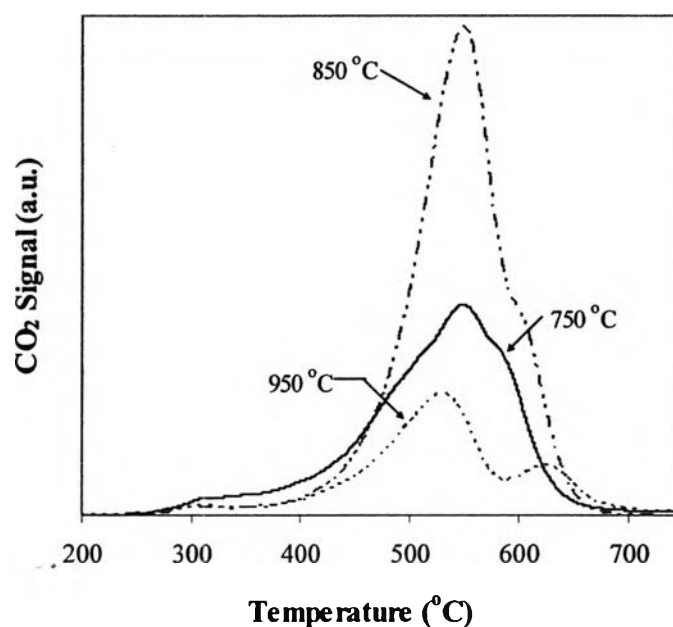


Figure 5.6 Temperature-programmed oxidation (TPO) of the carbon deposits obtained from the CO disproportionation at different reaction temperatures over Co-Re(1:4)/SiO₂ catalyst.

5.4.3 Effect of Co:Re Ratio

It is interesting to compare the amount of carbon deposited on the CoRe catalysts operated under the best operational conditions: a prereduction temperature of 800°C and a reaction temperature of 850°C. From Figure 5.7, the TPO profiles are 2.6, 3.5, and 5.8 wt %, over the catalysts containing the molar ratios of Co to Re, 2:1, 1:1, and 1:4, respectively. Under the studied conditions, a small

amount of disordered carbon generated during the reaction period was found to deposit on all catalysts. Furthermore, it is obvious that the molar ratio of Co to Re exhibits the less effect on the amount of disorder carbon, while both carbon yield and selectivity towards SWNTs are improved when using a low ratio of Co to Re.

The high-magnification TEM image of a fraction of deposited carbon obtained on a Co-Re(1:4)/SiO₂ sample with a pre-reduction temperature of 800°C and a reaction temperature of 850°C is shown in Figure 5.8. From the TEM image, the forms of deposited carbon were mainly found as small bundles of SWNTs, while undesired forms of carbon such as disordered carbon, MWNT, and graphitic carbon appeared in small quantities. It is interesting to note that most of the SWNTs produced at 850°C over Co-Re catalyst had an average tube diameter of 0.7 nm. The average bundle diameter was about 6 nm which is close to the pore size of silica support.

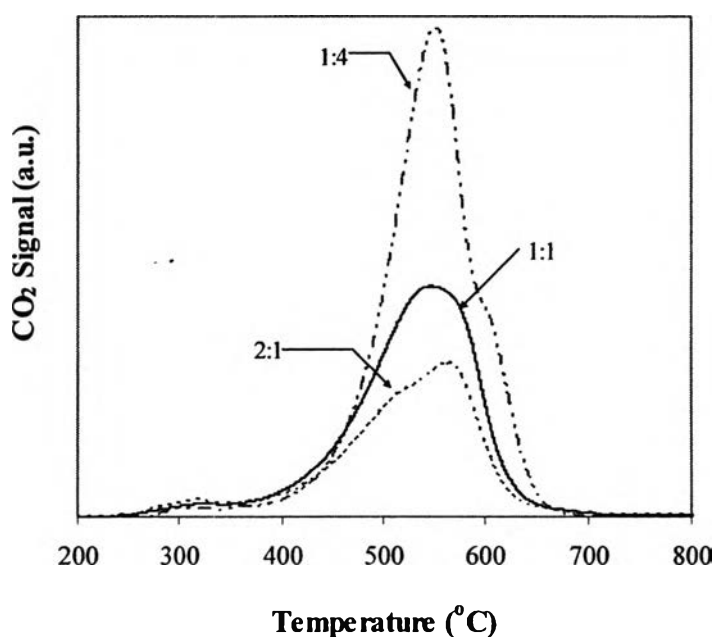


Figure 5.7 Temperature-programmed oxidation (TPO) of the carbon deposits obtained from the CO disproportionation at 850°C over different bimetallic Co-Re/SiO₂ catalysts.

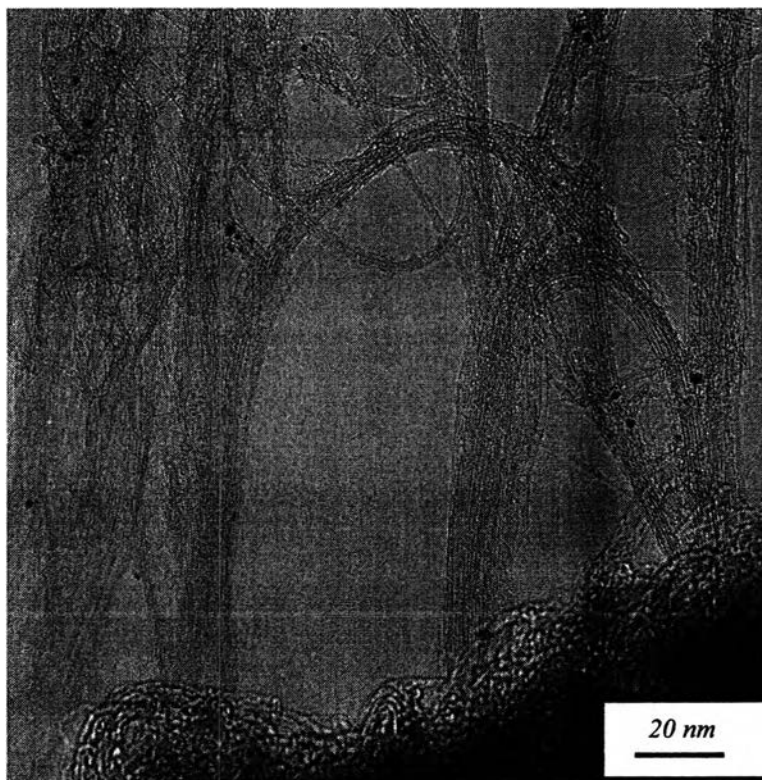


Figure 5.8 TEM image showing SWNTs produced by CO disproportionation at 850°C over Co-Re(1:4)/SiO₂ catalyst.

5.5 Conclusions

Silica-supported Co-Re catalysts were used for SWNTs synthesis using the CO disproportionation. The yield and selectivity towards SWNTs of Co-Re catalysts were found to strongly depend on the reduction temperature. The highest yield and selectivity were achieved with Co-Re(1:4)/SiO₂ when the catalyst was pretreated in H₂ at 800°C and the optimum reaction temperature was 850°C. The SWNTs obtained mainly consisted of 0.7-nm tubes which is the smallest diameter expected for capped SWNTs. At the optimum reduction temperature, all Co and Re oxides are completely reduced to metallic state at which the nanotubes are formed. However, the stabilization of Co species was found to occur in the Co-Re alloy phase, which is

different from what was observed in the Co-Mo/SiO₂ catalyst. To predict the mechanism on the Co-Re/SiO₂ catalyst, investigations will have to consider the interaction of Co and Re that are responsible for the nanotubes growth.

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